

Title	Improvement of Photovoltaic Performance in Microcrystalline Silicon Solar Cells
Author(s)	Chantana, Jakapan
Citation	
Issue Date	
oaire:version	
URL	https://hdl.handle.net/11094/59084
rights	
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氏 名	チャンタナ ジャカパン Chantana Jakapan
博士の専攻分野の名称	博 士 (工学)
学 位 記 番 号	第 2 5 2 3 8 号
学 位 授 与 年 月 日	平成 24 年 3 月 22 日
学 位 授 与 の 要 件	学位規則第4条第1項該当 基礎工学研究科システム創成専攻
学 位 論 文 名	Improvement of Photovoltaic Performance in Microcrystalline Silicon Solar Cells (微結晶シリコン太陽電池の性能改善に関する研究)
論 文 審 査 委 員	(主査) 教 授 岡本 博明 (副査) 教 授 高井 幹夫 教 授 酒井 朗

論 文 内 容 の 要 旨

A series of systematic studies has been carried out on material properties and device structures of hydrogenated microcrystalline silicon (μ c-Si:H) thin film solar cells at high rates (> 2 nm/s). In order to improve the photovoltaic performance in μ c-Si:H based substrate-type (n-i-p) solar cells, a wide variety of experimental issues has been conducted from the material deposition and characterization to the device fabrication and analysis of device operation.

The μ c-Si:H thin films deposited at high deposition rates (> 2 nm/s) by plasma-enhanced chemical vapor deposition (PECVD) process at low temperature are promising photovoltaic material in terms of low cost. High-quality μ c-Si:H with regard to film precursors and to the reactions on film-growing surfaces has been presented. The contribution ratio of short-lifetime reactive species (SiH_{ss}) to film growth radical (SiH_3), which is proportional to electron temperature (T_e) in the SiH_4/H_2 plasma, is the determining factors of the dangling-bond defect density (N_d) of the resulting film. In other word, the $[\text{SiH}_{\text{ss}}]/[\text{SiH}_3]$ density ratio, proportional to electron temperature (T_e), in the plasma should be minimized to obtain high-quality μ c-Si:H with low dangling-bond defect density (N_d) at high growth rates, prepared by PECVD at a fixed substrate

temperature (T_s). The optical-emission-intensity ratio of $I_{\text{Si}}^*/I_{\text{SiH}}^*$ could be used widely as a good measure of T_e in the plasma, which is a powerful tool to develop and characterize μ c-Si:H films at high rates directly in the SiH_4/H_2 plasma during film growth. I_{SiH}^* is proportional to the generation rate of SiH_3 -film precursors, being a good indicator of deposition rate of μ c-Si:H. Moreover, optical-emission-intensity ratio of $I_{\text{H}\alpha}/I_{\text{SiH}}^*$ during film growth has been used as a simple indicator to predict crystallinity (crystalline-volume fraction: X_c) in the resulting μ c-Si:H thin films. The relationship between $I_{\text{H}\alpha}/I_{\text{SiH}}^*$ and X_c has been checked under a wide variety of film-preparation conditions including low- (< 0.1 nm/sec) and high- (> 2 nm/sec) deposition-rate cases. On the basis of theoretical consideration, optical-emission-intensity ratio of $I_{\text{H}\alpha}/(I_{\text{SiH}}^*)^2$ has been proposed as a new indicator of X_c during film growth of μ c-Si:H.

When increasing the film growth rate, the optoelectronic properties in the resulting intrinsic μ c-Si:H films are severely deteriorated. The starting procedure of μ c-Si:H film growth at high rates (> 2 nm/s) has therefore been controlled in a very high frequency (VHF: 100 MHz) PECVD process to improve the optoelectronic properties of the resulting n/i interface as well as the intrinsic bulk layer in μ c-Si:H-based substrate-type (n-i-p) solar cells. The electron temperature, monitored using $I_{\text{Si}}^*/I_{\text{SiH}}^*$, in the plasma during film growth is successfully controlled by changing the starting procedure, i.e., gradual SiH_4 introduction or slow power application, leading to the preparation of high-quality μ c-Si:H films with a low dangling-bond defect density. Reduction of the defect density in the intrinsic layer and improvement of the optoelectronic properties at the n/i interface are demonstrated through the fabrication of single-junction n-i-p solar cells showing high photovoltaic performance.

As is well known that the photovoltaic performance of μ c-Si:H solar cells is also very much influenced by boron-doped p-type μ c-Si:H layer, much attention has been paid to the control of optoelectronic properties of p-type-window μ c-Si:H layer. The influence of B_2H_6 addition on the surface-reaction process during film growth has been investigated for the optimization of p-type μ c-Si:H layer prepared by Radio frequency (RF: 13.56 MHz) PECVD. Sticking probability (coefficient) of SiH_3 radical to the film-growing surface shows a drastic increase in the doping-ratio ($[\text{B}_2\text{H}_6]/[\text{SiH}_4+\text{B}_2\text{H}_6]$) range above 10^{-3} , explained by dangling-bond-defect production on the film-growing surface through the catalytic hydrogen- (H-) removal reaction with BH_3 chemical species. The same trend could be observed in the case of p-type (boron-doped) hydrogenated amorphous silicon (a-Si:H) growth, where most of hydrogen atoms do not reach the film-growing surface. This fact implies that a number of hydrogen atoms, supplied from the plasma under μ c-Si:H-growth condition, cannot cover surface-dangling bonds produced by H-removal reaction with BH_3 but act at subsurface region, leading to H-exchanging reactions for local heating. Moreover, the effects of temperature (during film growth and post-deposition thermal annealing) and hydrogen- (H-) plasma treatment on the electronic and structural properties of p- μ c-Si:H have been investigated for solar cell applications. The highest dark conductivity is obtained in the thermally annealed p- μ c-Si:H prepared at low substrate temperature. This dark conductivity is decreased by two orders of magnitude when the film is exposed to hydrogen plasma, being completely restored after thermal annealing. Namely, reversible dual-conductivity cycle is observed between thermally annealed state and hydrogen-plasma-treated state in p- μ c-Si:H. The dual-conductivity cycle is accompanied with the reversible change in the infrared-absorption spectrum at around 1845 cm^{-1} assigned as B-H-Si complex in p- μ c-Si:H network structure. Finally, a novel process to avoid the deterioration of photovoltaic performance in μ c-Si:H solar cells, prepared on the textured substrate with thin p-layer thickness, is proposed. The low temperature process for p-layer growth is performed to realize low defect density p-type layer as well as conformal p-layer coverage on highly textured i-layer surface. And post-deposition thermal annealing is carried out to increase electric conductivity through a thermal activation of 3-fold coordinated boron incorporated in the p layer deposited at low temperatures to 4-fold coordinated boron. Those are key points to improve photovoltaic performance in n-i-p type μ c-Si:H solar cells.

Light trapping plays an indispensable role in enhancing the photocurrent and efficiency. This is because μ c-Si:H has low optical absorption coefficient due to its indirect band gap. A novel type of substrate named “Ag-SP (surface plasmon) substrate”, in which silver nanoparticles are incorporated, is introduced and utilized as light trapping for μ c-Si:H solar cell in a substrate-type (n-i-p) configuration. Optical and morphological analyses of Ag-SP substrates fabricated with various sizes of silver nanoparticles are

systematically performed. It is shown that silver nanoparticles in Ag-SP substrate structure can lead to significant scattering of light when their diameter increases up to 300 nm. Furthermore, the photocurrent of the solar cell fabricated on an Ag-SP substrate with root-mean-square (RMS) roughness as small as 16.5 nm and a proper lateral diameter (approximately 300 nm) of silver nanoparticles is improved as compared to that of the solar cell prepared on reference textured substrate with RMS roughness of 25.3 nm, owing to strong scattering of light by silver nanoparticles in the red-infrared region.

論文審査の結果の要旨

本論文は、次世代太陽光発電技術を担うと期待されている微結晶シリコン太陽電池の性能改善を巡り、プラズマCVD製膜・デバイス形成プロセス科学技術探求からデバイス構成技術開発までの一連の研究成果をまとめたものである。本格的産業応用に向けた低コスト化・量産化には、シリコン薄膜の高速製膜が必要とされるが、本研究では、このような条件下で、高い太陽電池性能を確保するためのプラズマモニタリングに基づいた新規なプラズマ製膜プロセス制御法を提案している。

まず、CVDプラズマからの各種発光強度をその場観測することにより、n-i-p接合構成においてn層上に製膜される光電流活性i層の製膜速度、結晶分率や膜中欠陥密度を精緻に制御する手法を見いだしている。この発光分光法を駆使し、i層製膜初期プラズマを制御することによって、定常状態に達したプラズマ中での電子温度を低下させ、欠陥生成化学種の生成を抑制し、膜中欠陥密度を減少させて、2nm/secと言う極めて高い製膜速度環境で、ほぼ一桁低い製膜速度環境におけるのと同程度の太陽電池性能を得ている。また、n-i-p接合で最後に製膜されるp層に関して、低温製膜とその後の熱処理プロセスにより、電気的・光学的に高品位で均一なp層が得られることを実証し、この技術を適用して、高速製膜環境で、9%を超える世界最高レベルの太陽電池性能を達成している。さらに、薄膜系太陽電池では、必須とされる光閉じ込め手法について、局在表面プラズモンを活用した裏面光拡散層を世界で初めて開発し、長波長領域での光感度を飛躍的に増強させることに成功している。

上記のように、本研究は、プラズマCVDプロセスの原点に立ち戻って、微結晶シリコン太陽電池の性能改善を行ったもので、幾多の新規な学術的知見を示すとともに、当該領域の発展に資する技術指針を与えるもので、博士（工学）の学位論文として価値のあるものと認める。